Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

[enH][Cu_2AgSnS_4]: A Quaternary Layered Sulfide Based on Cu-Ag-Sn-S Composition

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Characterization

All reagents used in this study are analytical grade and commercially purchased from Alfa Aesar/Aldrich without further purification. Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer with a graphite-monochromatized Cu K_α radiation. The elemental analyses of Cu, Ag, Sn and S were carried out on an EDX-equipped JEOL/JSM-6360A SEM. Solid-state UV-Vis diffuse reflectance spectra were recorded at room temperature on powder samples with a Model UV-2501 PC. A $BaSO_4$ plate was used as a standard (100% reflectance). Thermogravimetric analysis was performed on a TGA Q2950 instrument under flowing N_2 with a heating rate of 10 °C /min.

Crystal X-ray crystallography

The single crystal X-ray diffraction data were collected on a SuperNova CCD diffractometer using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). All structures were solved by direct methods and refined by full-matrix least-squares cycles in SHELX-97. The ethylenediamine molecules are highly disordered and could not be fully located from the difference-Fourier maps, only two atoms (C1, N1), lying on a mirror plane, can be discerned from electron-density maps. CCDC number: 995740.

Electrode preparation

To prepare the photoelectrodes, 5 mg the samples of compound **1** were first ground using a marble mortar and pestle, and then added into 0.5 ml of 98% ethanol. The as-prepared solution was placed on a 60˚C hotplate stirrer overnight to ensure that the powders were completely dispersed in the solution. Meanwhile, the fluorine-doped tin oxide (F:SnO2, Tec 15, 10Ω/□, Hartford Glass Company) were cleaned thoroughly by sonication in 5% detergent for 30 min first and then rinsed with de-ionized water (DI water) for several times, which were followed by sonication in DI water for 15 min. The sonication in DI water process was repeated for three times. Before coating with samples, the FTO substrates were cleaned with UV-ozone plasma for 15 min to remove the organic residues. After that, 10 µl of the 10 mg/ml suspension of **1** was dropped onto the surface of FTO substrate, which was masked by a 3M scotch tape with an exposed area of 1.0 × 1.0 cm^2, and then dried in air at 60˚C on a hotplate. This step was repeated three times to achieve a uniform coverage of the samples on FTO.

Photoelectrochemical Measurements

The photoelectrochemical tests were performed using an electrochemical workstation (CHI 660B). A three-electrode set-up, with a platinum plate (1 × 2 cm^2) and a Ag/AgCl (in 3 M KCl) as the counter and reference electrodes, respectively, was used to study the biased photocurrent responses and linear sweep voltammetry. Meanwhile, the zero-biased photocurrent tests were carried out using a two-electrode set-up, in which the working electrode (compound 1/FTO) and the counter electrode (Pt) were short-circuited. 0.5 M sodium phosphate buffer (pH = 7.0) was used as the electrolyte throughout the photoelectrochemical tests. Prior to each measurement, the electrolyte was deaerated by purging it with argon continuously for 30 minutes. A 300 W Xenon lamp (Filtered, AM 1.5 G) was used as the standard light source, and the illumination intensity on the surface of the electrode was approximately 100 mW/cm^2.

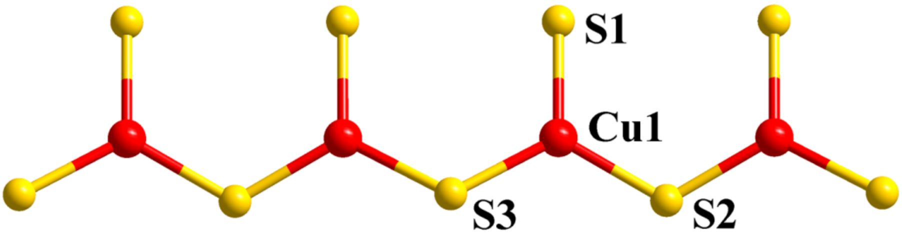

Figure S1. A $[Cu_2S_4]$ chain is built from $[CuS_3]$ trigonal planes via corner-sharing S2 and S3 atoms.

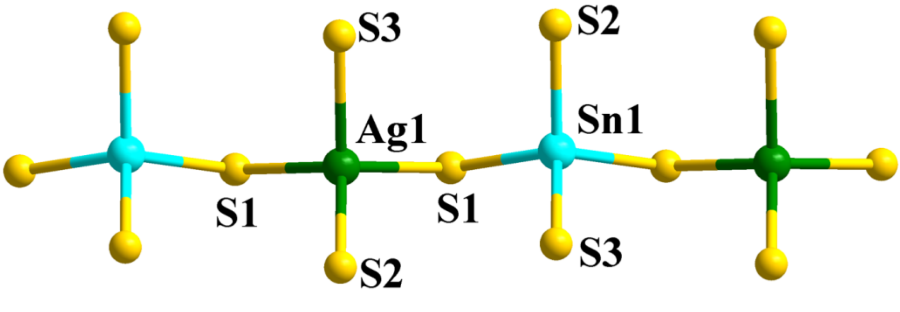

Figure S2. A $[AgSnS_6]$ chain is made up by alternately fusing $[AgS_4]$ and $[SnS_4]$ tetrahedrons at vertex-sharing S1 atoms.

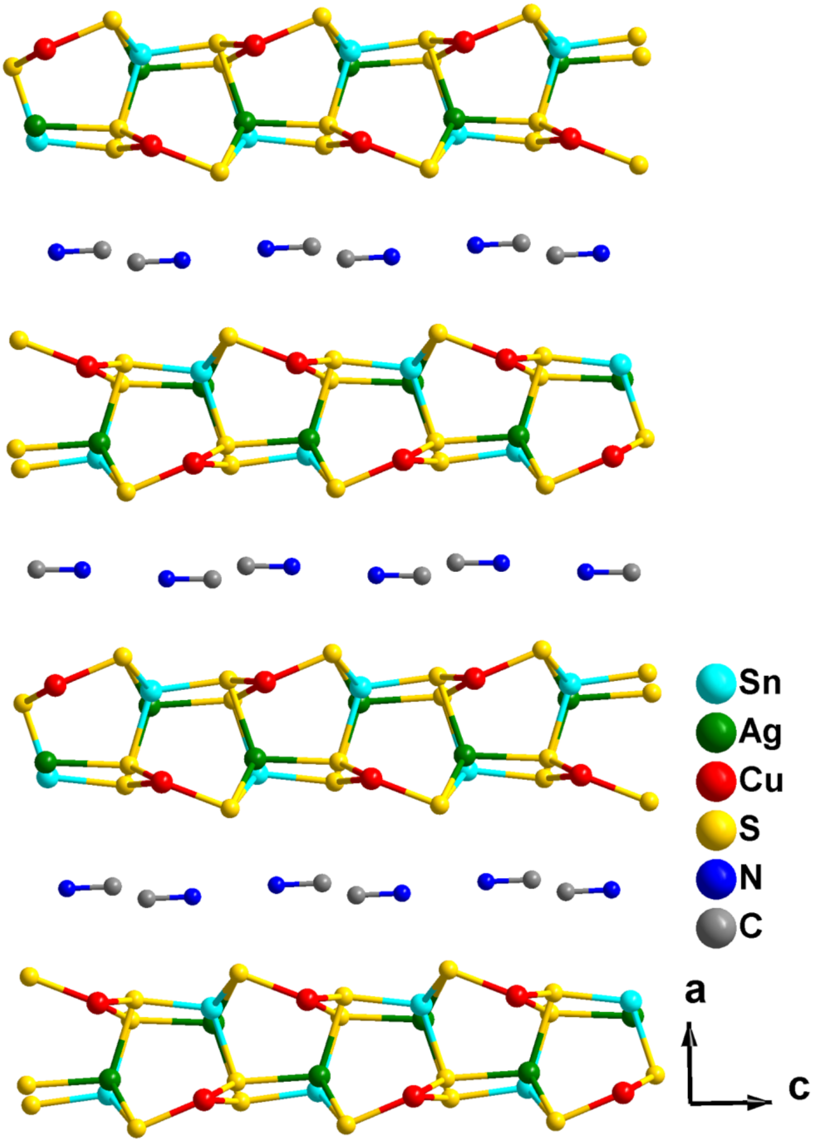

Figure S3. The anionic [Cu_2AgSnS_4]$^-$ layers are stacked in an ABAB sequence along the *a*-axis, where highly disordered ethylenediamine cations are located between the layers.

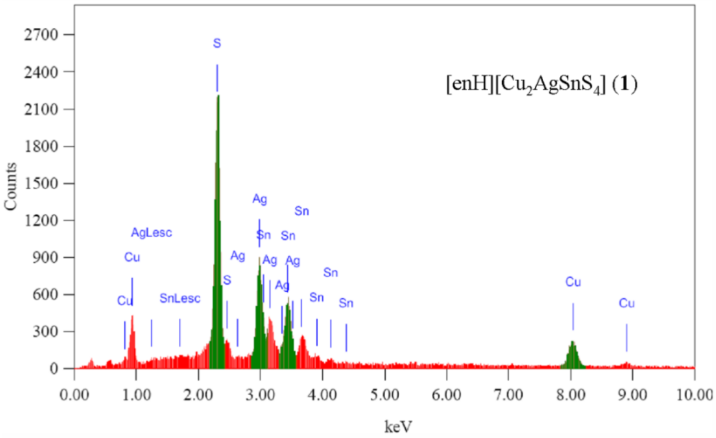

Figure S4. The energy dispersive X-ray (EDX) spectra of **1**. The calculated element percentage from the curve for Cu, Ag, Sn, S are 24.5/13.4/12.8/49.3.

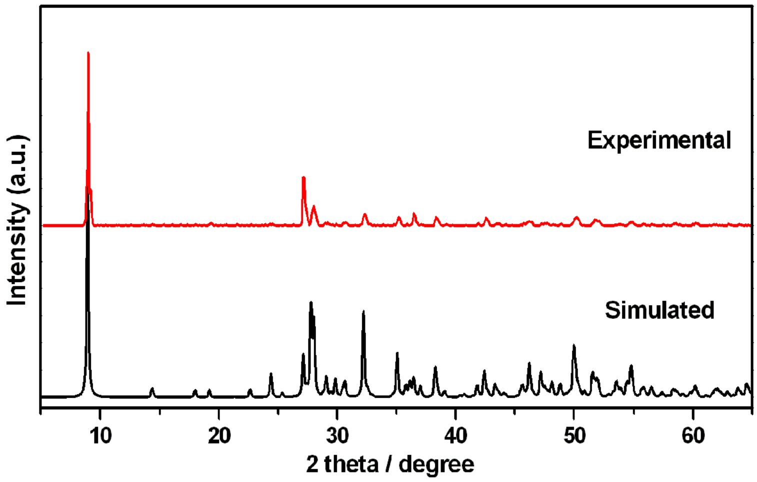

Figure S5. The experimental (red) and simulated (black) PXRD patterns of compound **1**.

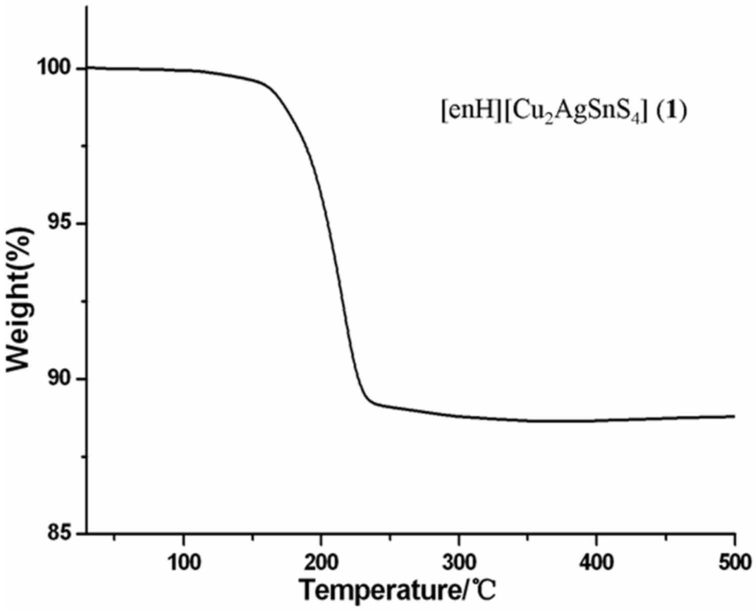

Figure S6. TGA curve of compound **1**.

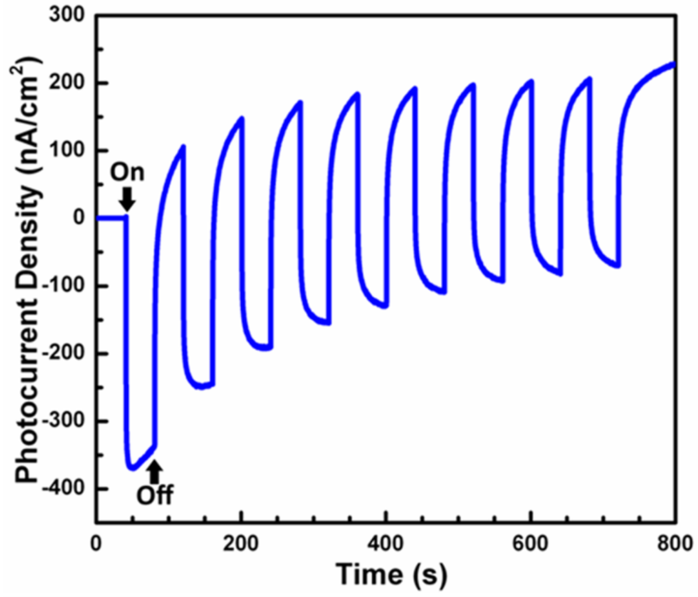

Figure S7. Photocurrent responses of **1**/FTO electrode upon chopped AM 1.5 G illumination with a bias at -0.3V vs Ag/AgCl.